

THESIS FOR THE DEGREE OF LICENTIATE OF ENGINEERING

Norbornadienes for Molecular Solar Thermal Energy Storage
Design, Synthesis and Characterization

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Cover:

Schematic illustration of norbornadiene and quadricyclane in a molecular solar thermal energy storage system

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Abstract

Over the last decade, there has been great scientific progress in terms of harvesting solar energy but the area of storing energy is still facing challenges. One approach to store solar energy is via photoinduced isomerization of chemical bonds, referred to as molecular solar thermal energy storage (MOST). Norbornadiene is a promising candidate molecule for this purpose, since upon irradiation isomerization occurs to form the metastable quadricyclane. The reaction is reversible and back conversion can be triggered to release the energy as heat. In this work, a new synthetic approach was developed to obtain 2-bromo-3-chloronorbornadiene that serves as an important starting material for further functionalization of norbornadienes. Through the developed procedure, a series of norbornadienes, decorated with electron donating and accepting substituents were synthesized. Photophysical characterization revealed that norbornadienes with cyano acceptor groups and ethynyl-substituted aromatic donor groups show a good solar spectrum match and high energy storage densities (296 – 545 kJ/kg). The obtained quantum yields for the photoisomerization processes were between 28 – 58% and the half-lives of the corresponding quadricyclanes in the range of 5 – 22 hours for the compounds with an ethynyl linker, and 55 days for the quadricyclane with similar substituents but without the ethynyl linker. The synthesized compounds illustrate the challenge in optimizing all parameters for an efficient MOST system in a single molecule system. For a deeper understanding of the relation between the structure and the properties, more variations of norbornadienes have to be synthesized and evaluated in future research.

Acknowledgements

First of all I would like to thank my supervisor Kasper Moth-Poulsen for choosing me for the position in his project, and also for always listening to me and keeping me motivated when things don't work out as planned (which is often the case in research :)). I would also like to thank Nina Kann, who recently became my co-supervisor, for all the good advices I got already.

Of course I would like to thank everyone that have been involved in the MOST – team and in the Moth-Poulsen group for being really nice colleagues. I would also like to thank the rest of you on the 8th floor for making it a nice place to go to.

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List of Publications

Paper I

A Convenient Route to 2-Bromo-3-chloronorbornadiene and 2,3-Dibromonorbornadiene. Lennartson A., Quant M., Moth-Poulsen K., *Synlett*, 2015, **26**, 1501-1504.

Paper II

Low Molecular Weight Norbornadiene Derivatives for Molecular Solar-Thermal Energy Storage. Quant M., Lennartson A., Dreos A., Kuisma M., Erhart O., Börjesson K., Moth-Poulsen K., *Chemistry – a European Journal*, 2016, **22**, 13265-13274.

Contribution Report

Paper I

Performed the synthesis of 2-bromo-3-chloronorbornadiene and 2,3-dibromonorbornadiene

Paper II

Performed the synthesis of most of the compounds, kinetic study of the back conversion, quantum yield measurements and wrote the manuscript.

List of Abbreviation

AM – air mass coefficient

Bu – butyl

HOMO – highest occupied molecular orbital

LUMO – lowest unoccupied molecular orbital

Me – methyl

MOST – molecular solar thermal energy storage

NBD – norbornadiene

NMP – n-methylpyrrolidone

NMR – nuclear magnetic resonance

THF – tetrahydrofuran

Ts – tosyl

QC – quadricyclane

QY – quantum yield

UV – ultraviolet

Vis – visible

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1. Introduction

For a sustainable future society, the fossil fuel consumption must decrease and be replaced by renewable energy sources. Hydroelectric power and wind turbines provide good alternative energy sources but the implementation is geographically restricted. Among the renewable energy sources, energy from sunlight is the most abundant and in just one hour the sun produces more energy than what is consumed in the entire world in one year.^[1] Over the last decade there has been great scientific progress in harvesting solar energy. Solar photovoltaics have been installed worldwide and in 2016 the capacity reached around 300 gigawatts.^[2] Also, improving solar cells is constantly ongoing research and the world record concerning the efficiency of a solar cell today is 46%.^[3] However, storing the solar energy is an area that still remains a great challenge. Despite successful strategies such as batteries,^[4] phase change materials,^[5] and storing as hydrogen through water splitting,^[6] this is not enough to meet the future energy demand.^[7] Since many of the known storage solutions are based on rare materials, new solar energy storage concepts based on abundant materials need to be developed. One approach that has not been explored to such a great extent is to store solar energy via photoinduced isomerization of chemical bonds, referred to as molecular solar thermal energy storage (MOST).^[8] In this approach, the solar energy is captured and stored in small molecules, which on demand can be triggered to release the energy as heat. This thesis concerns the development of new molecules for molecular solar thermal energy storage.

2. Molecular Solar Thermal Energy Storage

A molecular solar thermal energy storage system (MOST) is based on a compound that can undergo a sunlight induced conversion into a photoisomer.^[8] The absorbed energy is then stored in the photoisomer. When triggered with either heat or a catalyst, the energy is released as heat and the photoisomer is converted back to the parent compound (Figure 1). For a MOST system to be efficient, several requirements have to be fulfilled.^[9] First of all, the absorption profile of the parent compound must match the solar spectrum so the sun can drive the reaction, whereas the absorption of the photoisomer should not. If there is an overlap in absorption between the parent compound and the photoisomer, they will compete for the photons and the process will be less efficient. Secondly, the energy difference between the parent compound and the photoisomer ($\Delta H_{\text{storage}}$) should be large so that a large amount of energy can be stored in the system. At the same time, the activation energy for the back conversion (ΔH^\ddagger) should be high to ensure a long-lived photoisomer that can be stored for a period of time. Additionally, a fast photoisomerization reaction with high quantum yield and a robust system that can be used for many cycles are necessary.

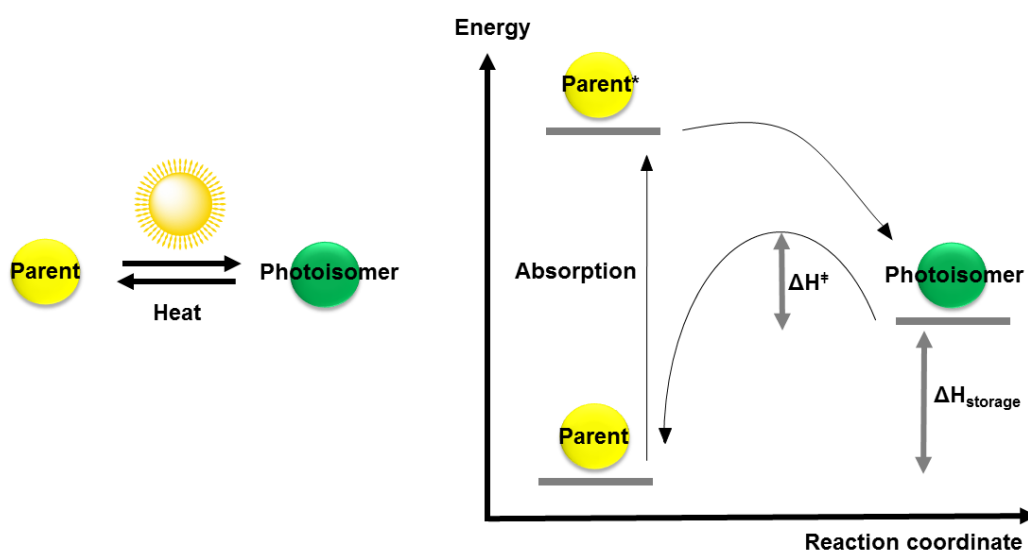


Figure 1. Illustration of a MOST system along with an energy diagram that illustrates the conversion of the parent compound to the photoisomer upon absorption of energy from light.

Several molecular systems have been evaluated and optimized as MOST candidates and some examples are displayed in Figure 2. The stilbene^[10] (Fig. 2a) and azobenzene^[11] (Fig. 2b) systems undergo an E – Z isomerization upon irradiation, while anthracene^[12] (Fig. 2c) forms a dimer and the fulvalene diruthenium^[13] rearranges (Fig. 2d). Dihydroazulene^[14] is converted

to the photoisomer vinylheptafulvene (Fig. 2e) and the norbornadiene is converted to a quadricyclane^[15] (Fig 2f). All these systems have different properties and therefore different advantages and disadvantages regarding their potentials as MOST candidates. However, this work is limited to the norbornadiene – quadricyclane system which will be further discussed in the following section.

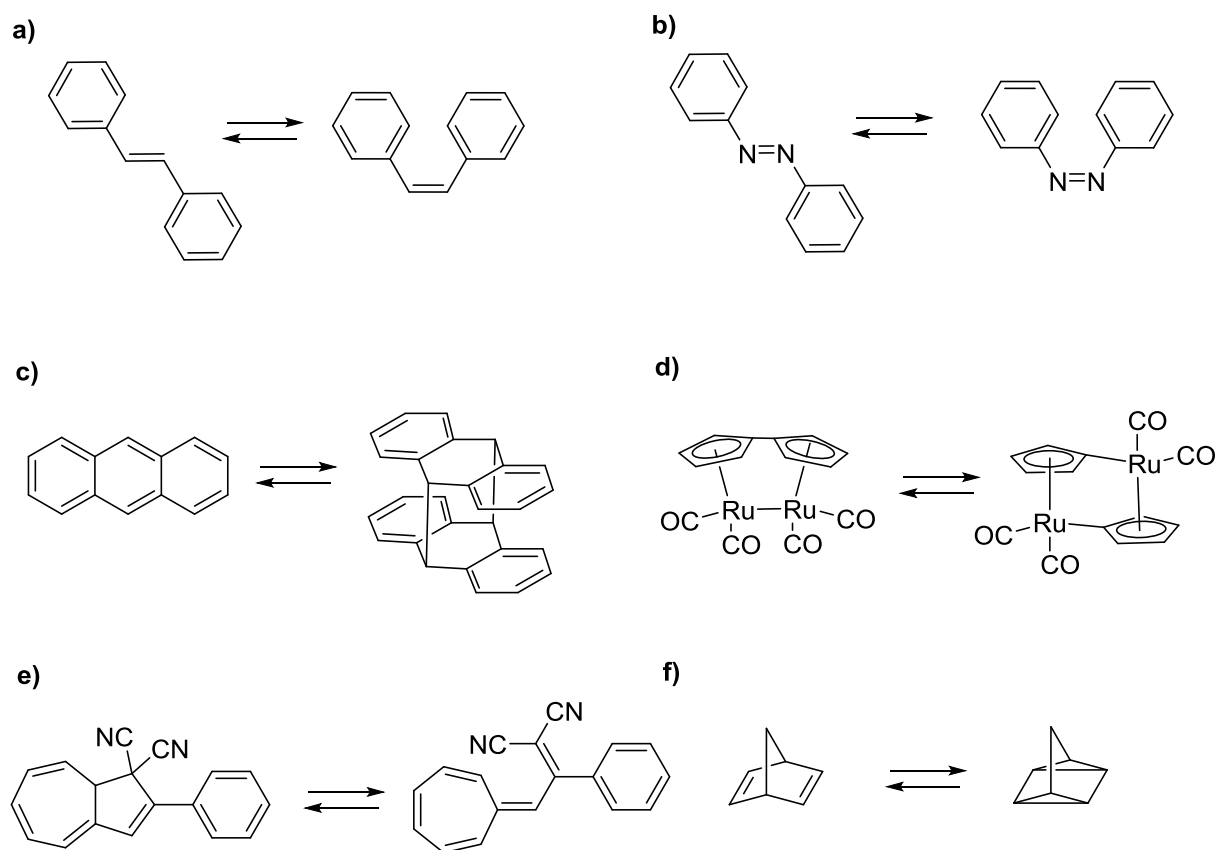
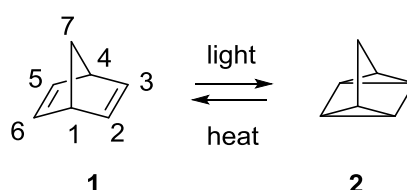


Figure 2. Molecular candidates for MOST applications and their photoisomerization processes **a)** stilbene and the E – Z isomerization process **b)** azobenzene and the E/Z isomerization process **c)** anthracene and the dimerization process **d)** tetracarbonyl-fulvalene-diruthenium and the photoisomerization **e)** dihydroazulene and the formation to the photoisomer vinylheptafulvene and **f)** norbornadiene and the formation of the photoisomer quadricyclane.

3. The Norbornadiene – Quadricyclane system

Norbornadiene (**1**) was first discovered in the beginning of the 1950s and is a rigid bridged cyclic organic compound that contains two double bonds. When norbornadiene is exposed to UV light, it undergoes a [2+2] cycloaddition and converts to the photoisomer quadricyclane (**2**) (Scheme 1).^[16] Quadricyclane is a highly strained compound that is metastable with higher energy than the norbornadiene. Therefore, the absorbed energy from light can be stored in the system, and when triggered with a catalyst or by heating the back conversion to norbornadiene can be induced and the energy released as heat.^[16a]



Scheme 1. Light induced photoisomerization of norbornadiene (**1**) into the photoisomer quadricyclane (**2**) and the back conversion using heat.

The unsubstituted norbornadiene – quadricyclane system (**1** and **2**) can store a large amount of energy with an energy storage density of around 90 kJ/mol corresponding to 980 kJ/kg.^[17] In addition, the energy barrier for the back conversion is high and the half-life of the quadricyclane is 14 hours at 140 °C thus the energy can be stored for a long period of time.^[16b] However, the main issue with this system is that the absorption onset for the norbornadiene is below 300 nm and therefore the sun cannot drive the reaction, which is a fundamental requirement for a MOST system. Also, the quantum yield is very low, around 5%.^[18] To achieve maximum solar energy conversion efficiency in a MOST system the quantum yield should be 100% and the ideal onset of absorption 656 nm.^[19]

The properties of the norbornadiene – quadricyclane system can be manipulated by introducing substituents to the system and to obtain a solar spectrum match the absorption has to be red-shifted. A successful strategy to red-shift the absorption is to introduce electron donating and electron accepting groups around the double bonds to create a push-pull system. Much research on donor/acceptor norbornadienes has been reported and two groups that have been particularly successful are the Yoshida group^[9a, 18, 20] and Dubonosov group^[15, 21]. Some examples of donor/acceptor norbornadienes are shown in Figure 3 where the groups can communicate through direct conjugation if introduced at the C2 and C3 positions (Fig. 3a), or through space via homo conjugation if located at the C2 and C6 positions (Fig. 3b). A great advantage with

such a system is that once the quadricyclane is formed, the conjugation will be lost and so will the connection between the donor and acceptor group, resulting in different absorption profiles for the norbornadiene and quadricyclane.

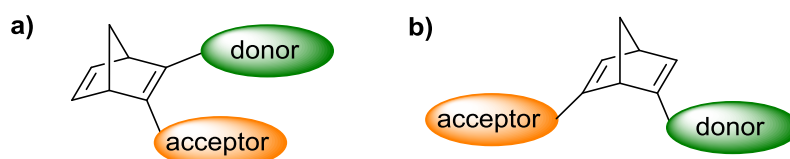


Figure 3. Norbornadiene with donor and acceptor group in **a)** the C2 and C3 positions **b)** the C2 and C6 positions.

Nevertheless, a trend in the system is that as the absorption of norbornadiene is red-shifted, the half-life of the quadricyclane tends to decrease and also lower the quantum yield. A series of diaryl substituted donor/acceptor norbornadienes were recently reported by our group and indeed they showed the same trend.^[22] One challenge is that optimizing one parameter results in negative effects on other parameters and for an efficient MOST system this issue has to be addressed. Therefore, more variants and new types of norbornadienes have to be prepared and evaluated for a deeper understanding of the correlation between the substitution pattern and the MOST properties.

4. Aim and Scope

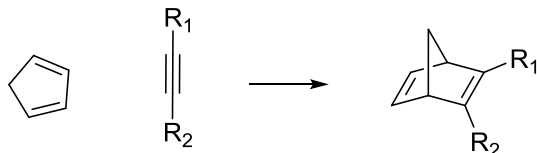
The aim of this thesis is to explore if it is possible to improve the performance of the norbornadiene – quadricyclane system by introducing donor/acceptor substituents at C2 and C3 position. In order to answer this research question, we set out to develop a new efficient synthetic protocol to obtain norbornadienes. Once a new norbornadiene has been synthesized the next step is to characterize the compound photophysically to explore the important requirements of a MOST system.

5. Experimental Methods

In this section, synthetic approaches toward norbornadienes and their photophysical characterization will be described, including the basics and experimental methods for absorption, quantum yield determination and the kinetics of the back conversion to determine the half-life.

5.1 Synthesis of Norbornadienes

Norbornadienes can be synthesized via the Diels-Alder reaction, which is a very useful transformation in organic synthesis to form cyclohexene derivatives from conjugated dienes and substituted alkenes or alkynes.^[23] The reaction was developed in 1928 by Otto Diels and Kurt Alder and in year 1950 they were rewarded with the Nobel Prize for their discovery.^[24] Unsubstituted norbornadiene (**1**) can be synthesized by reacting acetylene and cyclopentadiene in the Diels-Alder reaction, but also variations of the substrates can be used to introduce substituents in other positions of the norbornadiene.^[16a] One approach to make donor/acceptor norbornadienes is to react alkynes with both an electron donating (R_1) and electron accepting (R_2) group with cyclopentadiene as illustrated in Scheme 2.

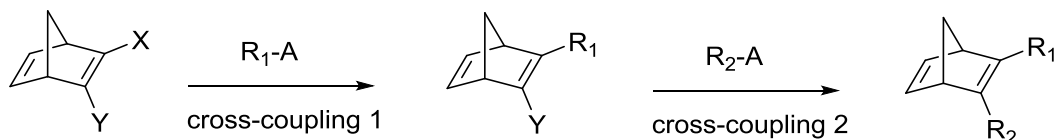


Scheme 2. Diels – Alder reaction to synthesize donor/acceptor norbornadienes. R_1 and R_2 represents donor and acceptor groups.

However, the scope of donor/acceptor norbornadienes that can be synthesized via Diels – Alder reaction is sometimes limited since the reaction normally requires electron deficient alkynes substituted with electron accepting groups and electron rich dienes substituted with electron donating groups. The opposite combination with an electron rich alkyne and electron deficient diene is also possible in the inverse kind, but using an alkyne decorated with both an electron donating and electron accepting group can be troublesome. Therefore, additional synthetic procedures must be developed in order to obtain all the desired variants of donor/acceptor norbornadienes.

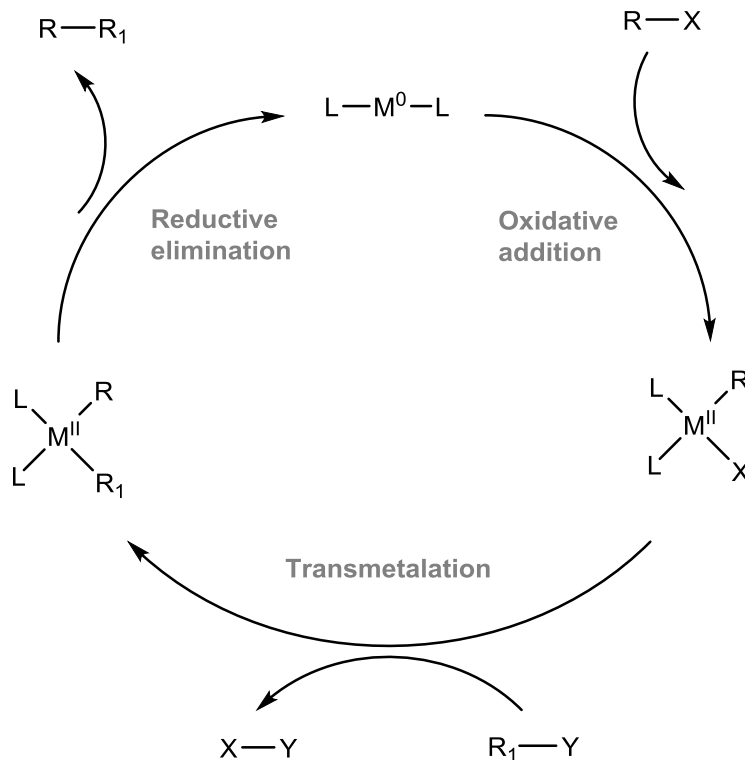
A different strategy is to introduce substituents via cross-coupling reactions using halogenated norbornadienes.^[25] As illustrated in Scheme 3, starting with a norbornadiene decorated with two different halogens (represented by X and Y) a cross-coupling reaction can be performed to

introduce either an electron donating or an electron accepting group (R_1). Thereafter, a second cross-coupling can be carried out to introduce the remaining group (R_2)



Scheme 3. Synthesis of donor/acceptor norbornadienes via cross-coupling reactions starting from halogenated norbornadienes. R_1 and R_2 represents donor and acceptor groups, X and Y different halogens and A the second coupling partner.

In cross-coupling reactions, different hydrocarbon fragments are connected using a metal catalyst. The general mechanism for such transformation is shown in Scheme 4.^[26] Generally, the coupling begins with an oxidative addition of one of the hydrocarbon fragments (R) to the metal catalyst. Thereafter, the other hydrocarbon fragment (R_1) binds to the metal in a transmetalation step. Finally, the coupled hydrocarbon fragments are released in a reductive elimination step and the catalyst is regenerated. Typically the metal catalyst is palladium and one of the hydrocarbons is an aryl halide or another type of organ halide.



Scheme 4. General mechanism for cross-coupling reactions.^[26]

The nature of the second hydrocarbon fragment can differ a lot; in the Heck^[27] reaction it is an alkene, in the Sonogashira^[28] coupling it is an alkyne, while in the Suzuki^[29] coupling it is a boronic acid. In other well-known coupling reactions such as the Stille^[30] coupling and the Negishi^[31] coupling, organotin and organozinc compounds are used as the second coupling partner. Because of the structural variety of the coupling partners in cross-coupling reactions, they are very useful in organic synthesis and can be utilized to synthesize many types of organic compounds.

5.2 Photophysical Characterization

5.2.1 Absorption and quantum yield measurements

When a photoactive compound is irradiated with electromagnetic radiation, it can absorb the energy, resulting in a transformation to a higher energy level thus the compound becomes excited. Once excited, several processes can take place; the compound can relax back to the ground state by emitting the energy via fluorescence or phosphorescence, the compound can go down to the ground state by vibrational relaxation (producing heat) or the absorbed energy can result in a chemical transformation as in the norbornadiene case (see Scheme 1, Section 3).

The absorption of a compound can be measured with a technique termed UV/Vis spectroscopy. In a typical UV/Vis spectroscopy experiment, a solution of the compound is exposed to light of different wavelengths and the fraction of the intensity of the incident and the transmitted light is measured to obtain the transmittance. The transmittance is correlated to the absorbance according to Equation 5.1, where T is the transmittance and A is the absorbance.

$$T = 10^{-A} \quad (5.1)$$

The absorbance can also be expressed by the molar extinction coefficient from the Lambert Beers Law (Equation 5.2), where A is the absorbance, ε the molar extinction coefficient, l is the path length of the light through the solution and c is the concentration.

$$A = \varepsilon \cdot l \cdot c \quad (5.2)$$

Therefore, by knowing the molar extinction coefficient of a compound, the concentration can be determined by simply measuring the absorbance, making UV/Vis spectroscopy a useful technique for monitoring reactions.

In the case where the absorption of light causes a chemical reaction, the efficiency is described by the quantum yield of the photoisomerization process. The quantum yield (ϕ) is defined as

the number of converted molecules ($n_{converted\ molecules}$) divided by the number of absorbed photons ($n_{absorbed\ photons}$) according to Equation 5.3.

$$\phi = \frac{n_{converted\ molecules}}{n_{absorbed\ photons}} \quad (5.3)$$

In a MOST system, it is important that the quantum yield is high, preferably close to unity, since otherwise photons will be wasted and the overall efficiency will be lowered.

The quantum yield can be measured by UV/Vis spectroscopy and the theory behind the experiment have been described in detailed by the Börjesson group.^[32] For a system like the norbornadiene – quadricyclane system, there are three processes that can occur simultaneously (Figure 4).

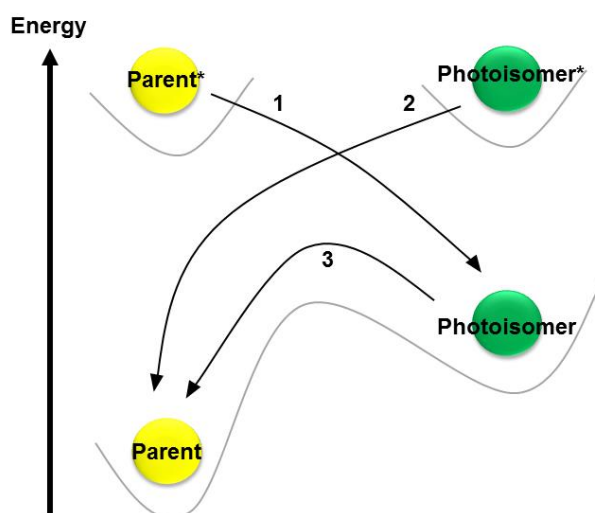


Figure 4. Three processes that can take place in a photoactive system. Process 1 and 2 illustrate the conversion of the parent compound to the photoisomer or vice versa after being excited by light. Process 3 illustrates the thermal conversion of the photoisomer back to the parent compound.

Upon irradiation, the parent compound (parent*) can be excited and photoisomerized to the photoisomer by process 1 or/and the excited photoisomer (photoisomer*) can be photoisomerized to the parent compound by process 2. In process 3, the photoisomer can be thermally converted to the parent compound, thus the rate equations of all three process are required to describe the photoisomerization process from the parent compound to the photoisomer (Equation 5.4), where, $[Parent]$ is the concentration of the parent compound, ϕ_{parent} and $\phi_{photoisomer}$ are the quantum yields for the photoisomerization process 1 and 2 respectively, I is the photon flux, β_{parent} and $\beta_{photoisomer}$ are the fractions of the absorbed photons by the parent compound and the photoisomers, N_A is Avogadro's number, V is the

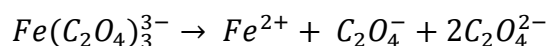
volume, k_t is the rate constant of the thermal conversion from the photoisomer to the parent compound and $[photoisomer]$ is the concentration of the photoisomer.

$$\frac{d[parent]}{dt} = -\frac{\phi_{parent} \cdot I \cdot \beta_{parent}(t)}{N_A \cdot I} + \frac{\phi_{photoisomer} \cdot I \cdot \beta_{photoisomer}(t)}{N_A \cdot I} + k_t [photoisomer] \quad (5.4)$$

However, the expression and also the measurements of the photoisomerization process of the parent compound to the photoisomer (process 1) can be simplified by making some assumptions. First of all, by performing the experiment at a low temperature, the thermal back conversion will not take place during the measurements and process 3 will be negligible. Secondly, by making a concentrated sample of the parent compound with an absorbance of over 2 at the irradiation wavelength, it can be assumed that more than 99% of the photons will be absorbed by the parent compound and almost none by the photoisomer. Consequently, process 2 will be negligible. By making these assumptions and applying the Lambert Beers law (Equation 5.2) to the rate expression (Equation 5.4), a linear dependence will be obtained (Equation 5.5) where, $[Parent]$ is the concentration of the parent compound, $[Parent]_0$ is the initial concentration of the parent compound, ϕ_{parent} is the quantum yield, I is the photon flux of, N_A is Avogadro's number, V is the volume and t_{irr} is the irradiation time.

$$[Parent] = [Parent]_0 - \frac{\phi_{parent} \cdot I}{N_A \cdot V} \cdot t_{irr} \quad (5.5)$$

Thus, the quantum yield can be obtained by stepwise irradiating the parent compound and measuring the decrease in concentration by UV/Vis spectroscopy. However, the photon flux of the irradiation source has to be known and since it can fluctuate and decrease with time, it should be determined prior to the quantum yield measurements. A way to measure the photon flux is by chemical actinometry,^[33] where the quantum yield of a photochemical process is known and can be used as reference. A commonly used actinometer is potassium ferrioxalate that decomposes upon irradiation (Scheme 5).



Scheme 5. Decomposition of potassium ferrioxalate upon irradiation.

The photon flux can be obtained by stepwise irradiating potassium ferrioxalate and measuring the amount of Fe^{2+} iron by reacting it with tris-phenanthroline to obtain a colored compound detectable in UV/Vis spectroscopy (Figure 5).^[32]

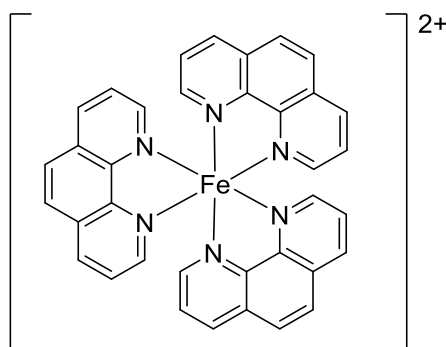


Figure 5. Complex of Fe^{2+} and phenanthroline.

5.2.2 Kinetic study of the back conversion

The rate of chemical reactions vary with temperature, and the correlation can be described either empirically by the Arrhenius equation (Equation 5.6) or by the Eyring equation, that follows from transition state theory (Equation 5.7), where k is the rate constant, A is constant for each chemical reaction, Ea is the activation energy, R is the universal gas constant, T is the absolute temperature, κ is the transmission coefficient, k_B is Boltzmann's constant, h is Planck's constant, ΔS^\ddagger is the entropy of activation and ΔH^\ddagger is the enthalpy of activation.

$$k = Ae^{-Ea/RT} \quad (5.6)$$

$$k = \frac{\kappa k_B T}{h} e^{(\Delta S^\ddagger/R)} e^{-(\Delta H^\ddagger/RT)} \quad (5.7)$$

The rate constant can be measured by UV/Vis spectroscopy, where the concentration of the formed species can be monitored. For a reaction that follows first order kinetics, the formation of the species (A) will have an exponential decay according to the integrated rate law (Equation 5.8), where $[A]$ is the concentration of the formed species, $[A]_0$ is the initial concentration, k is the rate constant and t is the reaction time.

$$[A] = [A]_0 e^{-kt} \quad (5.8)$$

The thermal back conversion of quadricyclane to norbornadiene follows first order kinetics, and information about the stability of the photoisomer can be gained by measuring the rate constants at different temperatures. If the rate constants at a range of temperatures are known, an Eyring plot can be constructed according to the linear form of equation 5.7 (equation 5.9) where the slope and intercept will provide information about the enthalpy and entropy of activation.

$$\ln\left(\frac{k}{T}\right) = -\frac{\Delta H^\ddagger}{R} * \frac{1}{T} + \ln\frac{K_B}{h} + \frac{\Delta S^\ddagger}{R} \quad (5.9)$$

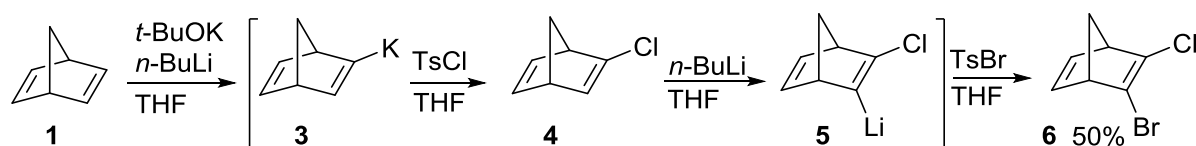
Furthermore, extrapolation of the Eyring plot can provide the rate constant at any temperature. The rate constant at 25 °C can be used to compare the stability of different quadricyclanes by calculating the half-life according to Equation 5.10, where, $t_{1/2}$ is the half-life and k is the rate constant.

$$t_{1/2} = \frac{\ln(2)}{k} \quad (5.10)$$

6. Results and Discussion

6.1 Synthesis of Donor/Acceptor Norbornadienes

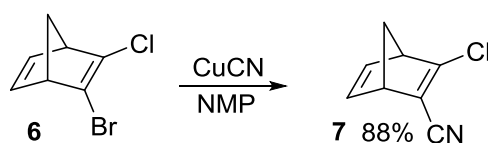
Halogenated norbornadienes are important starting materials for synthesizing donor/acceptor norbornadienes via cross-coupling reactions. Therefore, an efficient synthetic procedure towards 2-bromo-3-chloronorbornadiene (**6**) was developed (Scheme 6)



Scheme 6. Synthetic procedure towards 2-bromo-2-chloronorbornadiene.

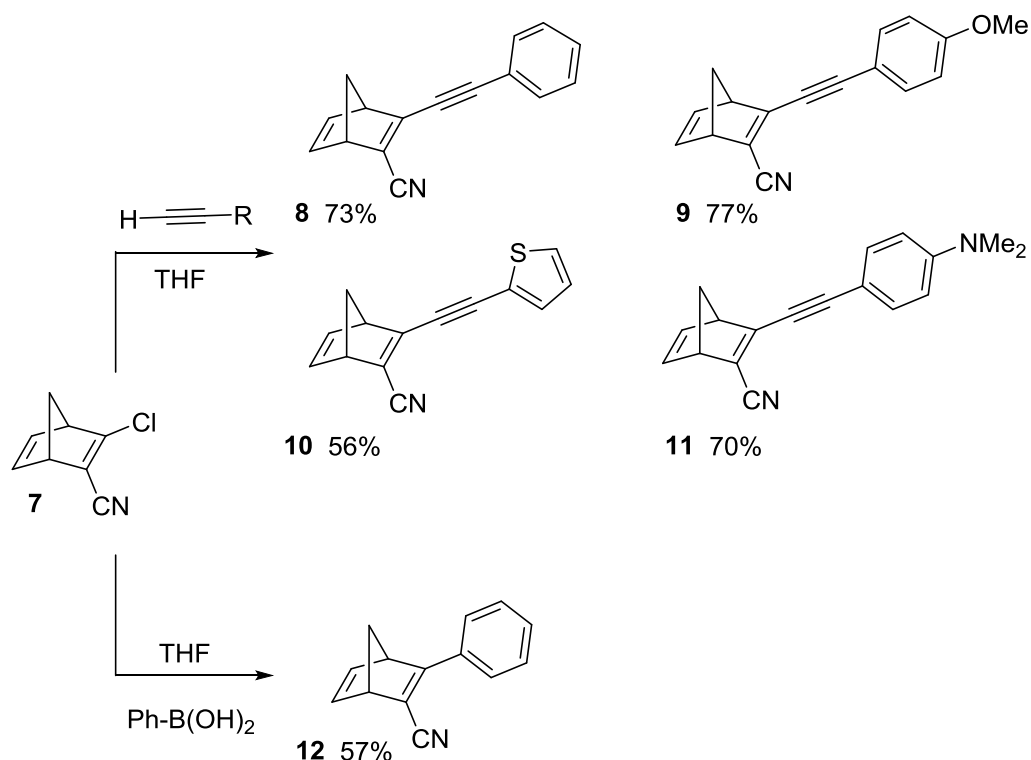
Starting from norbornadiene (**1**), potassium *tert*-butoxide and *n*-butyllithium were added to deprotonate, followed by the addition of with *p*-toluenesulfonyl chloride to introduce the chloride. Without isolation, 2-chloronorbornadiene (**4**) was deprotonated with *n*-butyllithium and reacted with *p*-toluenesulfonyl bromide to obtain **6** in an overall yield of 50%.

With 2-bromo-3-chloronorbornadiene (**6**) in hand, we were ready for making our donor/acceptor norbornadienes. Since the molecular weight affects the storage densities, it is important to have a low molecular weight. Therefore, we were interesting in making a series of compounds with a cyano functionality since it is one of the smallest electron accepting groups. By reacting **6** with copper(I)cyanide, 2-chloro-3-cyanonorbornadiene (**7**) was obtained at 88% yield based on consumed 2-bromo-3-chloronorbornadiene (Scheme 7.).



Scheme 7. Synthetic procedure towards 2-chloro-2-cyanonorbornadiene.

After forming **7**, a second substitution was carried out to introduce the electron donating group to the system. Through a Sonogashira cross-coupling reaction, a series of aromatic donor groups with an ethynyl linker were synthesized in yields of 73% for **8**, 77% for **9**, 56% for **10** and 70% for **11**. Additionally, to allow comparison between systems with and without ethynyl linker, 2-cyano-3-phenylnorbornadiene (**12**) was synthesized to a yield of 57% through a Suzuki cross-coupling reaction (Scheme 8).



Scheme 8. Synthetic procedure to obtain donor/acceptor norbornadienes via cross-coupling reactions.

6.2 Properties of Norbornadienes

6.2.1 Absorption

The UV/vis absorption spectra of norbornadienes **8** to **12** were recorded (Figure 6).

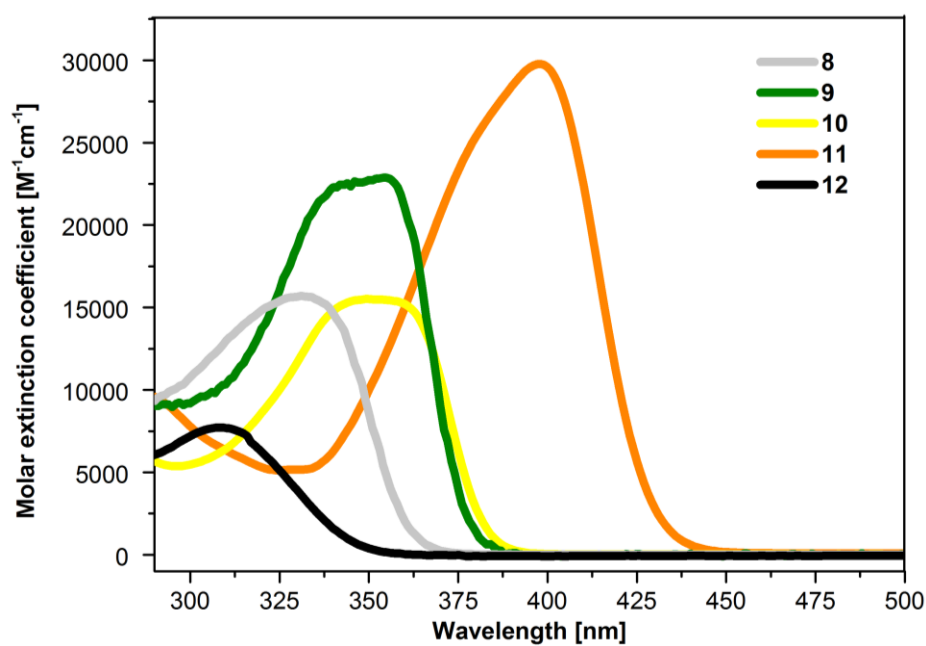


Figure 6. Absorption spectra for norbornadienes **8** – **12**.

Among the norbornadienes with an ethynyl linker, **11** has the best solar spectrum match with an absorption onset of 456 nm, and also the largest molar extinction coefficient. Norbornadienes **9** and **10** have similar absorption onsets of 391 and 395 nm respectively, whereas the onset of **8** is slightly lower at 374 nm. For **12**, i.e. the norbornadiene without an ethynyl linker, the onset is much lower at 358 nm and so is also the molar extinction coefficient. These results show that decorating the norbornadienes with an ethynyl linker between the norbornadiene core and the donor group is beneficial for increasing the molar extinction coefficient and also for red-shifting the absorption onset. Insights from electronic structure calculations suggests that the ethynyl linker between the donor groups and the norbornadienes minimizes the distortion of the conjugated π system, resulting in a red-shift in the absorption (comparing **8** and **12**). Additionally, the ethynyl linker enhances the dipole strength of the HOMO/LUMO transition, causing the large increase in the molar extinction coefficient. Donor groups such as thiophene and *p*-methoxyphenyl push the onset further towards the red region, but the best effect is obtained with the *p*-dimethylaminophenyl group as the donor group.

The norbornadienes were converted to their corresponding quadricyclanes (**13 – 17**) by irradiation and the photoisomerization processes were monitored by UV/Vis spectroscopy (Figure 7).

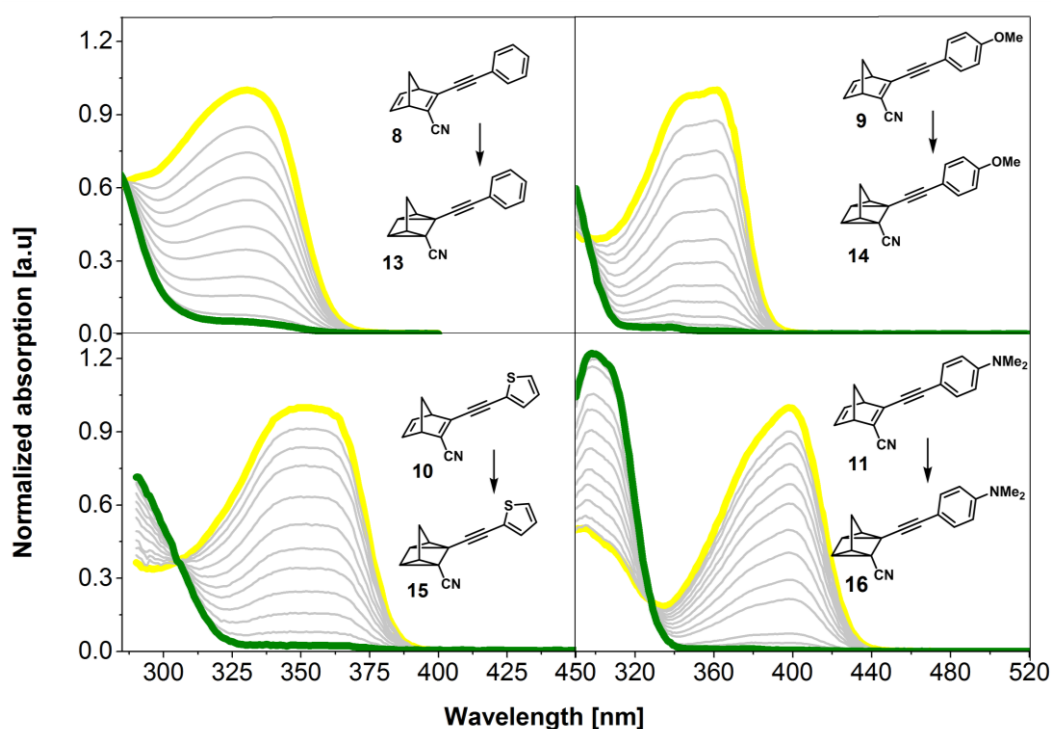


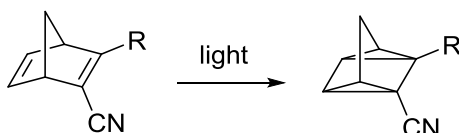
Figure 7. Photoisomerization processes of norbornadienes (**8 – 11** (yellow line)) to the corresponding quadricyclanes (**13 – 16** (green line)) monitored by UV/Vis spectroscopy. The samples were irradiated at 365 nm (**9 – 11**) and 310 nm (**8**).

For compound **8** there is a small overlap between the spectra of the norbornadiene and the quadricyclane, while this is not seen for the other compounds. For **11**, the corresponding quadricyclane does not absorb anything at all in the region where the norbornadiene absorbs which is a great advantage since there will be no competition of the photons between the two isomers. Isobestic points were obtained from the spectra for norbornadienes **8 – 11** and their corresponding quadricyclanes, indicating that only two species were present in the solutions. For **12** the expected isobestic point could not be observed due to overlap with the absorption onset of the solvent. Furthermore, to demonstrate that solar light can drive the isomerization process of these compounds, **11** was exposed to a 1.5 AM standard solar spectrum in a solar simulator. After about 10 seconds, **11** was fully converted to the corresponding quadricyclane **16**.

6.2.2 Quantum yield

The quantum yields for the photoisomerization processes were measured for all norbornadienes in toluene using potassium ferrioxalate as a chemical actinometer. The results are presented in Table 1 and show that the quantum yield was highest (58%) for **12**, i.e. the norbornadiene without an ethynyl linker. For compound **11**, the norbornadiene with the best solar spectrum match, the quantum yield was only 28%.

Table 1. Quantum yields for the conversion of norbornadienes **8 – 12** to quadricyclanes **13 – 17**.



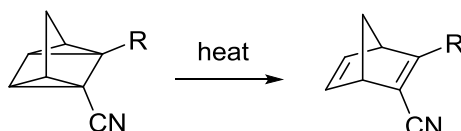
| Compound | Quantum Yield (%) |
|----------------|-------------------|
| 8 → 13 | 39 |
| 9 → 14 | 38 |
| 10 → 15 | 47 |
| 11 → 16 | 28 |
| 12 → 17 | 58 |

6.2.3 Half-life

In order to evaluate the half-lives of the photoisomers, a kinetic study was carried out. All norbornadienes were converted to their corresponding quadricyclanes by irradiation. The rate

of the back conversion was measured at six different temperatures for all compounds. The measured data show a linear trend in agreement with the Eyring equation for a unimolecular reaction mechanism (*For plots see the supporting information in paper II*). By extrapolation, the rate constant at 25 °C can be obtained and from that the half-life can be calculated. The results are presented in Table 2.

Table 2. Thermodynamic data for the thermal back conversion from quadricyclanes (**13 – 17**) to norbornadienes (**8 – 12**) along with the half-lives.



| Compound | Enthalpy of activation, ΔH^\ddagger (kJ/mol) | Entropy of activation, ΔS^\ddagger (J/Kmol) | Half-life at 25°C, $t_{1/2}$ (h) |
|-----------------------|---|--|-------------------------------------|
| 13 → 8 | 104 | 5.57 | 22.0 |
| 14 → 9 | 102 | 3.86 | 15.8 |
| 15 → 10 | 101 | 5.65 | 7.43 |
| 16 → 11 | 92.5 | -19.1 | 5.05 |
| 17 → 12 | 112 | -1.31 | 1320 |

The results show a major difference between the compounds with an ethynyl linker (**13 - 16**) and the one without this moiety (**17**). Quadricyclane **17** has a half-life of 55 days while the others have half-lives less than 24 hours. For quadricyclane **16**, the back conversion towards **11** is very rapid and proceeds in around 5 hours in room temperature.

6.2.4 Energy storage

The enthalpies of the back conversion from the quadricyclanes to the corresponding norbornadienes were measured by differential scanning calorimetry (Table 3). All compounds showed exothermic peaks and for **16** and **17**, one exothermic peak was obtained corresponding to a heat release of 103 and 122 kJ/mol which can be translated to an energy storage of 396 and 631 kJ/kg. For the other quadricyclanes, two exothermic peaks were obtained probably due to a complex phase behavior of a mixture of both norbornadienes and quadricyclanes. Therefore, it was not possible to precisely determine any values in these cases. The energy storage was also calculated by collaborators and for **16** and **17** the calculated energies show good agreement with the experimental observations.

Table 3. Measured and calculated storage enthalpies for the Back conversion of quadricyclanes (**13** – **17**) to norbornadienes (**8** – **12**).

| Compound | Measured Storage Enthalpies, $\Delta H_{\text{storage}}$ (kJ/kg) | Calculated Storage Enthalpies, $\Delta H_{\text{storage}}$ (kJ/kg) |
|-----------------------|---|---|
| 13 → 8 | - | 545 |
| 14 → 9 | - | 489 |
| 15 → 10 | - | 533 |
| 16 → 11 | 396 | 478 |
| 17 → 12 | 631 | 591 |

7. Conclusion and Future Work

In this thesis, donor/acceptor substituents were introduced at the C2 and C3 position of the norbornadiene – quadricyclane system to study the performance as a MOST candidate. In order to obtain norbornadienes, a new synthetic route towards 2-bromo-3-chloronorbornadiene was developed. The yield of the overall reaction was 50%, which is in the same range as previous published procedures.^[34] However, the great advantage with the new route is that the carcinogenic brominating agent 1,2-dibromoethane could be avoided, and also the synthesis is easy to scale up and can be performed in one day without isolating the intermediates. With 2-bromo-3-chloronorbornadiene in hand, a new series of donor/acceptor norbornadienes were synthesized through a cyanation step followed by a Sonogashira or Suzuki cross-coupling reaction. Photophysical characterization revealed that norbornadienes with cyano acceptor groups and ethynyl-substituted aromatic donor groups (**8** – **11**) show a good solar spectrum match with absorption onsets of 374 to 456 nm and high energy storage densities between 396 and 545 kJ/kg. However, as the ethynyl linker is introduced, the half-life and the quantum yield decreases, which becomes clear when comparing norbornadienes **8** and **12**. Thus, introducing such donor/acceptor substituents at C2 and C3 positions improves some MOST qualities while others are worsen. This study illustrates the challenge in optimizing all parameters at once and therefore it may be necessary to have more specific MOST application in mind. For example, norbornadienes similar to **11** could be perfect candidates for day to night storage, where a long half-life is not essential. Compounds with poor solar spectrum match such as **12**, may still be utilized for MOST applications if combined with other techniques such as photon upconversion,^[35] a process where photons of long wavelength are converted to photons with higher energy.

For future work, more variants of norbornadienes have to be synthesized in order to gain a deeper understanding of how the structure is related to the properties. Since this work was published, co-workers in our research group have been investigating new series of norbornadienes containing triazole functionalities,^[36] substituents on the bridge head position (C7 in Scheme 1, Section 3),^[37] norbornadiene oligomers,^[38] hetroaryl-linked norbornadiene dimers,^[39] and an expanded series of norbornadienes with a cyano moiety.^[40] This work shows promising strategies on how to improve quantum yields, half-lives and storage densities but the picture is still not completely clear. Therefore, there is still a demand for making more norbornadienes to gain a deeper understanding. Also, to complement experimental studies with

theoretical calculations is of great interest since some structure/properties relations can be predicted.^[41]

Furthermore, it may also be of interest to investigate the potential of other molecular systems such as stilbene, azobenzene, and anthracene (see Figure 2, Section 2), or brand new systems that have not yet been explored for storing solar energy. A recent publication by the Bettinger group described a new type of compound for storing energy, a boron-nitrogen benzene derivative that can photoisomerize to a Dewar isomer.^[42]

Additionally, new synthetic methods should be explored, since the overall goal with MOST is to contribute to a sustainable society. Thus, the synthesis has to be environmentally friendly and also the nature of the starting materials has to be considered. For real device applications, larger amounts of material are needed and scaling up the process will be necessary. In this case, using rare metals such as palladium will neither be environmentally friendly or cost effective.

Finally, exploring solvent effects on the norbornadiene – quadricyclane system is of great interest. Some promising MOST compounds are solids at standard conditions and have to be dissolved for characterization or lab scale device testing. In recent work from our group, liquid norbornadienes were explored. The norbornadienes were able to photoisomerize, which is a great step toward high energy density solvent free MOST systems, but the half-lives changed from hours to minutes when passing from solution to neat samples.^[43] Consequently, for some future applications, solvents will be necessary. An ongoing study has indicated that the choice of solvent does not only affect the half-lives of the quadricyclanes, but also the isomerization process. To further explore this topic will be one of the projects for the author's upcoming research.

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